PH 422: Quantum Mechanics II
Tutorial Sheet 5

This tutorial sheet contains problems related to the time-dependent perturbation theory.

1. Suppose that the matrix element $\langle i|V|n\rangle$ which occurs in the Fermi's Golden Rule, is zero for a given quantum mechanical system. This means that the transition rate $\Gamma_{n\to i} = 0$, in the first order of perturbation theory. Compute the corresponding transition rate in the second order of time-dependent perturbation theory. Assume, as before that the perturbation term V has no explicit time dependence.
Soln: Second-order perturbation theory expression for the coefficient is

$$i\hbar\frac{da_i^{(2)}}{dt} = \sum_j V_{ij}(t)e^{iE_{ij}t/\hbar}a_j^{(1)}(t), \tag{1}$$

where $E_{ij} = E_i - E_j$. We know that for cases, when the system was in state $|\psi_n\rangle$, initially $(t = 0)$

$$a_i^{(1)}(t) = \frac{1 - e^{iE_{in}t/\hbar}}{E_{in}}V_{in}. \tag{2}$$

Substituting $a_j^{(1)}$ from Eq. 2 in Eq. 1, we obtain

$$\begin{aligned} i\hbar\frac{da_i^{(2)}}{dt} &= \sum_j \frac{V_{ij}V_{jn}e^{iE_{ij}t/\hbar}(1 - e^{iE_{jn}t/\hbar})}{E_{jn}} \\ &= \frac{1}{i\hbar}\sum_j \frac{e^{iE_{ij}t/\hbar}}{E_{jn}}V_{ij}V_{jn} - \frac{1}{i\hbar}\sum_j \frac{e^{iE_{in}t/\hbar}}{E_{jn}}V_{ij}V_{jn} \\ \implies a_i^{(2)}(t) &= \sum_j \frac{V_{ij}V_{jn}}{i\hbar E_{jn}}\int_0^t e^{iE_{ij}t'}dt' - \sum_j \frac{V_{ij}V_{jn}}{i\hbar E_{jn}}\int_0^t e^{iE_{in}t'}dt' \\ &= \sum_j V_{ij}V_{jn}\left\{\frac{1 - e^{iE_{ij}t/\hbar}}{E_{ij}E_{jn}} - \frac{1 - e^{iE_{in}t/\hbar}}{E_{in}E_{jn}}\right\}. \end{aligned} \tag{3}$$

Next we compute the probability of transition

$$\begin{aligned} P_{n\to i}^{(2)}(t) &= |a_i^{(2)}(t)|^2. \\ &= \left[\sum_j V_{ij}V_{jn}\left\{\frac{1 - e^{iE_{ij}t/\hbar}}{E_{ij}E_{jn}} - \frac{1 - e^{iE_{in}t/\hbar}}{E_{in}E_{jn}}\right\}\right] \\ &\times \left[\sum_k V_{ik}^*V_{kn}^*\left\{\frac{1 - e^{-iE_{ik}t/\hbar}}{E_{ik}E_{kn}} - \frac{1 - e^{-iE_{in}t/\hbar}}{E_{in}E_{kn}}\right\}\right] \\ &= \sum_{j,k} V_{ij}V_{jn}V_{ik}^*V_{kn}^*\left\{\frac{(1 - e^{iE_{ij}t/\hbar})(1 - e^{-iE_{ik}t/\hbar})}{E_{ij}E_{jn}E_{ik}E_{kn}}\right. \\ &- \frac{(1 - e^{iE_{ij}t/\hbar})(1 - e^{-iE_{in}t/\hbar})}{E_{ij}E_{jn}E_{in}E_{kn}} - \frac{(1 - e^{iE_{in}t/\hbar})(1 - e^{-iE_{ik}t/\hbar})}{E_{in}E_{jn}E_{ik}E_{kn}} \\ &+ \left.\frac{(1 - e^{iE_{in}t/\hbar})(1 - e^{-iE_{in}t/\hbar})}{E_{in}E_{jn}E_{in}E_{kn}}\right\} \\ &= \sum_{j,k} V_{ij}V_{jn}V_{ik}^*V_{kn}^*\left\{\frac{(1 - e^{iE_{ij}t/\hbar} - e^{-iE_{ik}t/\hbar} + e^{iE_{kj}t/\hbar})}{E_{ij}E_{jn}E_{ik}E_{kn}}\right. \\ &- \frac{(1 - e^{iE_{ij}t/\hbar} - e^{-iE_{in}t/\hbar} + e^{iE_{nj}t/\hbar})}{E_{ij}E_{jn}E_{in}E_{kn}} - \frac{(1 - e^{iE_{in}t/\hbar} - e^{-iE_{ik}t/\hbar} + e^{iE_{kn}t/\hbar})}{E_{in}E_{jn}E_{ik}E_{kn}} \\ &+ \left.\frac{4\sin^2\frac{E_{in}t}{2\hbar}}{E_{in}^2E_{jn}E_{kn}}\right\} \end{aligned} \tag{4}$$

The required transition rate is

$$\Gamma^{(2)}_{n\to i} = \lim_{t\to\infty} \frac{P^{(2)}_{i\to n}(t)}{t} \tag{5}$$

On using the expression for $P^{(2)}_{n\to i}(t)$ from Eq. 4, constant terms will go to zero on taking the limit, while remaining time-dependent terms will average out to zero, except the last term which will lead to energy conserving Dirac delta function as shown below

$$\lim_{t\to\infty}\left(\frac{\sin^2\frac{E_{in}t}{2}}{E^2_{in}}\right) = \frac{\pi t}{2\hbar}\delta(E_i - E_n).$$

Thus using this relation in conjunction with Eq. 4, in Eq. 5, we obtain

$$\begin{aligned}\Gamma^{(2)}_{n\to i} &= \frac{2\pi}{\hbar}\sum_{j,k}\frac{V_{ij}V_{jn}V^*_{ik}V^*_{kn}}{E_{jn}E_{kn}}\delta(E_i - E_n)\\ &= \frac{2\pi}{\hbar}\left(\sum_j \frac{V_{ij}V_{jn}}{E_{jn}}\right)\left(\sum_k \frac{V^*_{ik}V^*_{kn}}{E_{kn}}\right)\delta(E_i - E_n)\\ &= \frac{2\pi}{\hbar}\left|\sum_j \frac{V_{ij}V_{jn}}{E_{jn}}\right|^2 \delta(E_i - E_n).\end{aligned}$$

This is Fermi's Golden rule in the second-order perturbation theory.

2. Consider a one-dimensional harmonic oscillator of mass m, angular frequency ω_0, and charge q. We know that for this system $H_0|n\rangle = (n+\frac{1}{2})\hbar\omega_0|n\rangle$. Assume that it is subject to the following perturbation

$$V(t) = \begin{cases} -qEx & \text{for } 0 \le t \le \tau \\ 0 & \text{for } t < 0 \text{ and } t > \tau, \end{cases}$$

where $\mathcal{E}$ is the electric field. If $P_{n\to i}$ is the transition probability from the initial level n to the final level i, then

(a) compute $P_{0\to 1}$ as a function of τ

(b) Show that in the first order of perturbation theory $P_{0\to 2} = 0$

(c) Compute $P_{0\to 2}$ in the second order of perturbation theory.

Soln: We know that assuming $a_{j(0)} = \delta_{j,n}$, we have to the first order

$$a^{(1)}_i(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i(E_i - E_n)\frac{t}{\hbar}} V_{in}(t')$$

but

$$\begin{aligned}V_{in}(t') &= -qE\langle i|x|n\rangle \quad for \quad 0 \le t \le \tau\\ &= 0 \qquad\qquad\qquad otherwise\end{aligned}$$

using

$$\langle i|x|n\rangle = \sqrt{\frac{\hbar}{m\omega}}\left[\sqrt{\frac{i}{2}}\delta_{n,i-1} + \sqrt{\frac{i+1}{2}}\delta_{n,i+1}\right]$$

we have

$$a^{(1)}_i(\tau) = -\sqrt{\frac{\hbar}{m\omega}}\left[\sqrt{\frac{i}{2}}\delta_{n,i-1} + \sqrt{\frac{i+1}{2}}\delta_{n,i+1}\right] \times \frac{\left\{e^{i(E_i - E_n)\frac{\tau}{\hbar}} - 1\right\}}{E_i - E_n}$$

$$\Rightarrow P^{(1)}_{n\to i}(\tau) = |a^{(1)}_i(\tau)|^2.$$

$$= \frac{\hbar}{m\omega}\left[\frac{i}{2}\delta_{n,i-1} + \left(\frac{i+1}{2}\right)\delta_{n,i+1}\right] q^2E^2 \times \left(\frac{\sin\frac{E_{in}\tau}{2\hbar}}{\frac{E_{in}}{2}}\right)^2 \tag{6}$$

Using $E_{in} = (i-n)\hbar\omega$, we have

$$P^{(1)}_{n\to i}(\tau) = \frac{\hbar q^2E^2}{m\omega}\left\{\frac{i}{2}\delta_{n,i-1} + \left(\frac{i+1}{2}\right)\delta_{n,i+1}\right\}\left(\frac{\sin\frac{(i-n)\omega\tau}{2}}{\frac{(i-n)\hbar\omega}{2}}\right)^2$$

$$P^{(1)}_{n\to i}(\tau) = \frac{4q^2E^2}{m\hbar\omega^3}\frac{\sin^2\frac{(i-n)\omega\tau}{2}}{(i-n)^2}\left\{\frac{i}{2}\delta_{n,i-1} + \left(\frac{i+1}{2}\right)\delta_{n,i+1}\right\} \tag{7}$$

(1). From Eq.(7) it is obvious that when $n=0$, only possible value of $i=1$.

$$\Rightarrow P_{0\to1}(\tau) = \frac{4q^2E^2}{2m\hbar\omega^3}\sin^2\frac{\omega\tau}{2}$$

$$\boxed{P_{0\to1}(\tau) = \frac{2q^2E^2}{m\hbar\omega^3}\sin^2\frac{\omega\tau}{2}}$$

(2). From Eq.(7) it is obvious that $P_{0\to2}(\tau)=0$, because both Kronecker deltas will yield zero. That is $V_{20}\propto\langle 2|x|0\rangle = 0$

(3). We will have to derive the result in the second order of perturbation theory. From the previous problem

$$a^{(2)}_i(\tau) = \sum_j\left\{\frac{V_{ij}V_{jn}(1-e^{iE_{ij}\tau/\hbar})}{E_{ij}E_{jn}} - \frac{V_{ij}V_{jn}(1-e^{iE_{in}\tau/\hbar})}{E_{in}E_{jn}}\right\}$$

for $n=0$ and $i=2$ only one intermediate state $j=1$ will give nonzero V_{ij} and V_{jn}.We have

$$V_{21} = -qE\sqrt{\frac{\hbar}{m\omega}}$$

$$V_{10} = -qE\sqrt{\frac{\hbar}{2m\omega}}$$

$$\Rightarrow a^{(2)}_i(\tau) = \frac{q^2E^2\hbar}{m\omega\sqrt{2}}\left\{\frac{(1-e^{i\omega\tau})}{\hbar^2\omega^2} - \frac{(1-e^{2i\omega\tau})}{2\hbar^2\omega^2}\right\}$$

$$= \frac{q^2E^2}{m\hbar\omega^3\sqrt{2}}\left\{\frac{(1-e^{i\omega\tau})}{1} - \frac{(1-e^{2i\omega\tau})}{2}\right\}$$

$$
\begin{aligned}
\Rightarrow P^{(2)}_{0\to2}(\tau) &= |a^{(2)}_i(\tau)|^2 \\
&= \frac{q^4E^4}{2m^2\hbar^2\omega^6}\left\{(1-e^{i\omega\tau}) - \frac{(1-e^{2i\omega\tau})}{2}\right\} \times \left\{(1-e^{-i\omega\tau}) - \frac{(1-e^{-2i\omega\tau})}{2}\right\} \\
&= \frac{q^4E^4}{2m^2\hbar^2\omega^6}\left\{(1-e^{i\omega\tau} - e^{-i\omega\tau} + 1 + \frac{1}{4}(2-e^{2i\omega\tau}-e^{2i\omega\tau})\right. \\
&\quad \left. -\frac{(1-e^{-2i\omega\tau}-e^{i\omega\tau}+e^{-i\omega\tau})}{2} - \frac{(1-e^{-i\omega\tau}-e^{2i\omega\tau}+e^{i\omega\tau})}{2}\right\} \\
&= \frac{q^4E^4}{2m^2\hbar^2\omega^6}\left\{4\sin^2\frac{\omega\tau}{2} + \sin^2\omega\tau - \frac{(2-e^{-2i\omega\tau}-e^{-2i\omega\tau})}{2}\right\} \\
&= \frac{q^4E^4}{2m^2\hbar^2\omega^6}\left\{4\sin^2\frac{\omega\tau}{2} + \sin^2\omega\tau - 2\sin^2\omega\tau\right\} \\
&= \frac{q^4E^4}{2m^2\hbar^2\omega^6}\left\{4\sin^2\frac{\omega\tau}{2} - \sin^2\omega\tau\right\} \\
&= \frac{q^4E^4}{2m^2\hbar^2\omega^6}4\sin^2\frac{\omega\tau}{2}\left\{1-\cos^2\frac{\omega\tau}{2}\right\}
\end{aligned}
$$

or

$$
\boxed{P^{(2)}_{0\to2}(\tau) = \frac{2q^4E^4}{m^2\hbar^2\omega^6}\sin^4\frac{\omega\tau}{2}}
$$

3. Consider two spin 1/2's, $\mathbf{S}_1$ and $\mathbf{S}_2$, interacting with each other through Hamiltonian $H(t) = a(t)\mathbf{S}_1\cdot\mathbf{S}_2$; where $a(t)$ is a function of time which satisfies $\lim_{|t|\to\infty} a(t) = 0$, and takes on non-negligible values (of the order of a_0) only inside an interval τ, symmetrically placed about $t=0$.

   (a) At $t=-\infty$, the system is in the state $|+,-\rangle$. Calculate, without approximations, the state of the system at $t=+\infty$. Show that probability $P(+-\to-+)$ of finding, at $t=+\infty$, the system in the state $|-,+\rangle$, depends only on the integral $\int_{-\infty}^{+\infty} a(t)dt$.
   Soln: We expand the time dependent wave function, as usual, in terms of the four eigenfunctions of the initial Hamiltonian $H_0 = a(t\to-\infty)\mathbf{S}_1\cdot\mathbf{S}_2 = 0$. Thus, we can treat the basis states (using the $|jm\rangle$ notation)

$$
\begin{aligned}
|\psi^0_1\rangle &= |00\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) \\
|\psi^0_2\rangle &= |11\rangle = |++\rangle \\
|\psi^0_3\rangle &= |10\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \\
|\psi^0_4\rangle &= |1-1\rangle = |--\rangle,
\end{aligned}
$$

   as eigenfunctions of H_0 with eigenvalues $E_i = 0$. Therefore, we can write the $|\psi(t)\rangle$ as

$$
|\psi(t)\rangle = \sum_{i=1}^{4} c_i(t)|\psi^0_i\rangle.
$$

   Substituting this in the time-dependent Schrödinger equation $i\hbar\frac{d|\psi(t)\rangle}{dt} = H(t)|\psi(t)\rangle$, we obtain

$$
i\hbar\sum_i \frac{dc_i}{dt}|\psi^0_i\rangle = a(t)\sum_i c_i(t)\mathbf{S}_1\cdot\mathbf{S}_2|\psi^0_i\rangle. \tag{8}
$$

   Because states $|\psi^0_i\rangle$ are eigenfunctions of $\mathbf{S}_1\cdot\mathbf{S}_2 = \frac{1}{2}\left(\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2\right) = \frac{1}{2}\left(\mathbf{S}^2 - \frac{3}{2}\hbar^2 I\right)$, with eigenvalues given by

$$
\frac{1}{2}(\mathbf{S}^2 - \frac{3}{2}\hbar^2 I)|\psi^0_i\rangle = e_i|\psi^0_i\rangle,
$$

$$
\text{where } e_i = \begin{cases} -\frac{3}{4}\hbar^2 \text{ for } i=1 \\ \frac{1}{4}\hbar^2 \text{ for } i=2-4 \end{cases}
$$

we obtain in Eq. 8

$$i\hbar\sum_i \frac{dc_i}{dt}|\psi_i^0\rangle = a(t)\sum_i c_i(t)e_i|\psi_i^0\rangle.$$

Because $|\psi_i^0\rangle$ form an orthonormal set, from above we obtain the first-order differential equation for $c_i(t)$

$$\begin{aligned}\frac{dc_i}{dt} &= -\frac{i}{\hbar}a(t)c_ie_i \\ \frac{dc_i}{c_i} &= -\frac{i}{\hbar}e_ia(t)dt \\ c_i(t) &= c_i(-\infty)e^{-\frac{ie_i}{\hbar}\int_{-\infty}^t a(t')dt'}\end{aligned}$$

But, it is given

$$\begin{aligned}|\psi(t=-\infty)\rangle = |+-\rangle &= \frac{1}{\sqrt{2}}\left(|\psi_1^0\rangle + |\psi_3^0\rangle\right) \\ \implies c_1(-\infty) &= \frac{1}{\sqrt{2}} \\ c_3(-\infty) &= \frac{1}{\sqrt{2}} \\ \text{and } c_i(t) = 0 &\quad \text{for } i = 2, 4\end{aligned}$$

Thus, at time t

$$\begin{aligned}|\psi(t)\rangle &= \frac{1}{\sqrt{2}}\left\{e^{3i\hbar(\int_{-\infty}^t a(t')dt')/4}|\psi_1^0\rangle + e^{-i\hbar(\int_{-\infty}^t a(t')dt')/4}|\psi_3^0\rangle\right\} \\ &\text{on discarding the common phase} \\ |\psi(t)\rangle &= \frac{1}{\sqrt{2}}\left\{|\psi_1^0\rangle + e^{-i\hbar(\int_{-\infty}^t a(t')dt')}|\psi_3^0\rangle\right\}.\end{aligned}$$

This is the exact solution of the time-dependent Schrödinger equation for this case. Now the desired probability as a function of time is

$$P(+- \to -+, t) = |\langle -+|\psi(t)\rangle|^2 = |-\frac{1}{2} + \frac{1}{2}e^{-i\hbar(\int_{-\infty}^t a(t')dt')}|^2 = \sin^2\frac{\hbar\int_{-\infty}^t a(t')dt'}{2}.$$

On taking the limit $t \to \infty$, the desired probability is

$$P(+- \to -+) = \sin^2\frac{\hbar\int_{-\infty}^{\infty} a(t)dt}{2},$$

which clearly depends only on the integral $\int_{-\infty}^{\infty} a(t)dt$.

(b) Calculate the same probability using the first-order perturbation theory, and compare your results with those obtained in the preceding part.
Soln: For perturbation theory calculations $H_0 = a(-\infty)\mathbf{S}_1 \cdot \mathbf{S}_2 = 0$, therefore, we can take the basis states

$$\begin{aligned}|\psi_1^0\rangle &= |++\rangle \\ |\psi_2^0\rangle &= |+-\rangle \\ |\psi_3^0\rangle &= |-+\rangle \\ |\psi_4^0\rangle &= |--\rangle\end{aligned}$$

as eigenfunctions of H_0 with eigenvalues $E_i = 0$. Here the initial state $|\psi_n\rangle = |+-\rangle = |\psi_2^0\rangle$ and the final state $|\psi_i\rangle = |-+\rangle = |\psi_3^0\rangle$, and the perturbation $V(t) = a(t)\mathbf{S}_1 \cdot \mathbf{S}_2$. In the first order of perturbation theory

$$c_3^{(1)}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} dt^{'} V_{32}(t^{'}) = \frac{\langle\psi_3^0|\mathbf{S}_1\cdot\mathbf{S}_2|\psi_2^0\rangle}{i\hbar}\int_{-\infty}^{t} dt^{'} a(t^{'})$$

using the representations of $\mathbf{S}_1 \cdot \mathbf{S}_2$, $|\psi_2^0\rangle$, $|\psi_3^0\rangle$

$$\langle\psi_3^0|\mathbf{S}_1\cdot\mathbf{S}_2|\psi_2^0\rangle = \frac{\hbar^2}{4}(0,0,1,0)\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \frac{\hbar^2}{2}, \quad \text{so that}$$

$$c_3^{(1)}(t) = \frac{\hbar}{2}\int_{-\infty}^{t} a(t')dt'$$

and

$$P^{(1)}(+- \to -+, t) = |c_3(t)|^2 = \frac{\hbar^2}{4}\left(\int_{-\infty}^{t} a(t')dt'\right)^2$$

leading to

$$P^{(1)}(+- \to -+) = \frac{\hbar^2}{4}\left(\int_{-\infty}^{\infty} a(t')dt'\right)^2,$$

which is nothing but the first-order term in the Taylor expansion of the exact value of probability obtained in part (a).

4. The unperturbed Hamiltonian of a two-level system is represented by

$$H_0 = \begin{pmatrix} E_1^0 & 0 \\ 0 & E_2^0 \end{pmatrix}.$$

This system is perturbed by a time-dependent term

$$V(t) = \begin{pmatrix} 0 & \lambda\cos\omega t \\ \lambda\cos\omega t & 0 \end{pmatrix},$$

where λ is real.

(a) At $t = 0$, the system is known to be in the first state, represented by

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

Using time-dependent perturbation theory, and assuming that $|E_1^0 - E_2^0| \gg \hbar\omega$, derive an expression for the probability that the system be found in the second state represented by

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

as a function of t ($t > 0$).

Soln: From the structure of H_0 it is obvious that its eigenvalues are E_i^0, with the corresponding eigenfucntions $|\psi_i^{(0)}\rangle$ given by

$$|\psi_1^{(0)}\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|\psi_2^{(0)}\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Now in the first order of perturbation theory

$$a_i^{(1)}(t) = \frac{1}{i\hbar}\sum_j \int_{t_0}^{t} dt^{'} c_j e^{i(E_i^0 - E_j^0)t^{'}/\hbar} V_{ij}(t^{'})$$

where $a_i^{(0)}(t = t_0) = c_i$. Here $t_0 = 0$, and $a_i^{(0)}(0) = \delta_{i1}$, and we want to calculate $a_2^{(1)}(t)$. From above it is obvious

$$\begin{aligned}
a_2^{(1)}(t) &= \frac{1}{i\hbar}\int_0^t dt^{'}\, e^{i(E_2^0 - E_1^0)t^{'}/\hbar V_{21}(t^{'})} \\
&= \frac{\lambda}{i\hbar}\int_0^t dt^{'}\, e^{i(E_2^0 - E_1^0)t^{'}/\hbar}\cos\omega t \\
&= \frac{\lambda}{2i\hbar}\int_0^t dt^{'}\,\left\{e^{i(E_2^0 - E_1^0)t^{'}/\hbar + i\omega t} + e^{i(E_2^0 - E_1^0)t^{'}/\hbar - i\omega t}\right\} \\
&= \frac{\lambda}{2}\left(\frac{1 - e^{i(E_{21}^0 + \hbar\omega)t/\hbar}}{E_{21}^0 + \hbar\omega} + \frac{1 - e^{i(E_{21}^0 - \hbar\omega)t/\hbar}}{E_{21}^0 - \hbar\omega}\right).
\end{aligned}$$

where $E_{21}^0 = E_2^0 - E_1^0$. Required transition probability is

$$\begin{aligned}
P_{1\to 2}(t) &= |a_2^{(1)}(t)|^2 \\
&\frac{\lambda^2}{4}\left[\left\{\frac{2 - e^{i(E_{21}^0 + \hbar\omega)t/\hbar} - e^{-i(E_{21}^0 + \hbar\omega)t/\hbar}}{(E_{21}^0 + \hbar\omega)^2}\right\} + \left\{\frac{2 - e^{i(E_{21}^0 - \hbar\omega)t/\hbar} - e^{-i(E_{21}^0 - \hbar\omega)t/\hbar}}{(E_{21}^0 - \hbar\omega)^2}\right\}\right. \\
&\left. + \frac{(1 - e^{i(E_{21}^0 + \hbar\omega)t/\hbar})(1 - e^{-i(E_{21}^0 - \hbar\omega)t/\hbar})}{(E_{21}^0 + \hbar\omega)(E_{21}^0 - \hbar\omega)} + \frac{(1 - e^{-i(E_{21}^0 + \hbar\omega)t/\hbar})(1 - e^{i(E_{21}^0 - \hbar\omega)t/\hbar})}{(E_{21}^0 + \hbar\omega)(E_{21}^0 - \hbar\omega)}\right] \\
&= \frac{\lambda^2}{4}\left[\frac{4\sin^2(E_{21}^0 + \hbar\omega)t/2\hbar}{(E_{21}^0 + \hbar\omega)^2} + \frac{4\sin^2(E_{21}^0 - \hbar\omega)t/2\hbar}{(E_{21}^0 - \hbar\omega)^2}\right. \\
&\left. + \frac{(2 - 2\cos(E_{21}^0 + \hbar\omega)t/\hbar - 2\cos(E_{21}^0 - \hbar\omega)t/\hbar + 2\cos 2\omega t)}{(E_{21}^0 + \hbar\omega)(E_{21}^0 - \hbar\omega)}\right]
\end{aligned}$$

The numerator of the last term above can be written as

$$\begin{aligned}
&(2 - 2\cos(E_{21}^0 + \hbar\omega)t/\hbar) + (2 - 2\cos(E_{21}^0 - \hbar\omega)t/\hbar) - (2 - 2\cos 2\omega t) \\
&= 4\sin^2(E_{21}^0 + \hbar\omega)t/2\hbar + 4\sin^2(E_{21}^0 - \hbar\omega)t/2\hbar - 4\sin^2\omega t,
\end{aligned}$$

leading to the final result

$$\begin{aligned}
P_{1\to 2}(t) = \lambda^2 &\left[\frac{\sin^2(E_{21}^0 + \hbar\omega)t/2\hbar}{(E_{21}^0 + \hbar\omega)^2} + \frac{\sin^2(E_{21}^0 - \hbar\omega)t/2\hbar}{(E_{21}^0 - \hbar\omega)^2}\right. \\
&\left. + \frac{\sin^2(E_{21}^0 + \hbar\omega)t/2\hbar + \sin^2(E_{21}^0 - \hbar\omega)t/2\hbar - \sin^2\omega t}{(E_{21}^0 + \hbar\omega)(E_{21}^0 - \hbar\omega)}\right]
\end{aligned}$$

(b) Why is this procedure not valid when $|E_1^0 - E_2^0| \approx \hbar\omega$?
Soln: The procedure is not valid for the resonant condition $|E_1^0 - E_2^0| \approx \hbar\omega$, because then the denominators of the above expression for probability become zero, leading to an unphysical infinite value.

5. Consider a three-level system where the unperturbed states are of the form $|j, m\rangle$, with $j = 1$, and $m = 0, \pm 1$. We define the ordered orthonormal basis as $|\psi_1\rangle = |1, -1\rangle$, $|\psi_2\rangle = |1, 0\rangle$, and $|\psi_3\rangle = |1, 1\rangle$,with $\langle\psi_i|\psi_j\rangle = \delta_{ij}$, where $|\psi_i\rangle$ are eigenfunctions of the time-independent Hamiltonian H_0

$$\begin{aligned}
H_0|\psi_1\rangle &= (E_0 - \hbar\omega_0^{'})|\psi_1\rangle \\
H_0|\psi_2\rangle &= E_0|\psi_2\rangle \\
H_0|\psi_3\rangle &= (E_0 + \hbar\omega_0)|\psi_1\rangle.
\end{aligned}$$

The degeneracy of the $j = 1$ states has been broken by applying external magnetic and electric fields. Next, a radio frequency field rotating at the angular velocity ω in the xOy plane is applied, leading to the time-dependent perturbation

$$V(t) = \frac{\omega_1}{2}\left(J_+ e^{-i\omega t} + J_- e^{i\omega t}\right),$$

where ω_1 is a constant.

(a) Assuming that

$$|\psi(t)\rangle = \sum_{i=1}^{3} a_i(t) e^{-iE_i t/\hbar}|\psi_i\rangle,$$

write down the differential equations satisfied by $a_i(t)$.

Soln: We showed in the lectures that the equation satisfied by $a_i(t)$ is

$$\frac{da_i(t)}{dt} = \frac{1}{i\hbar}\sum_j V_{ij} a_j(t) e^{\frac{i(E_i - E_j)t}{\hbar}} \tag{9}$$

(b) Assume that $|\psi(t=0)\rangle = |\psi_1\rangle$. Show that if we want to calculate $a_3(t)$ by time-dependent perturbation theory, the calculation must be pursued to second order.

Soln: We showed in the lectures that with the initial condition $|\psi(0)\rangle = |\psi_1\rangle \Rightarrow a_j(0) = \delta_{j1}$, the solutions of Eq.(9) to the first and second order perturbation theory will be proportional to

$$a_3^{(1)}(t) \propto V_{31}(t)$$

but it is obvious that for

$$V(t) = \frac{\omega_1}{2}\left(J_+ e^{-i\omega t} + J_- e^{i\omega t}\right)$$
$$V_{13}(t) = 0$$

$\Rightarrow$calculations must be pursed for higher orders.

(c) Compute $a_3(t)$ up to second order of perturbation theory. For fixed t, how does the probability $P_{1\to 3}(t) = |a_3(t)|^2$ vary with respect to ω? Show that a resonance appears, not only for $\omega = \omega_0$ and $\omega = \omega_0'$, but also for $\omega = (\omega_0 + \omega_0')/2$.

Soln: We will first need to derive $a_i^{(1)}(t)$ and then $a_i^{(2)}(t)$. We know for $a_i(0) = \delta_{in}$, we have

$$a_i^{(1)}(t) = \frac{1}{i\hbar}\int_0^t dt' \, e^{i(E_i - E_n)t'/\hbar} V_{in}(t')$$

but

$$V_{in}(t') = \frac{\omega_1}{2} e^{-i\omega t}\langle i|J_+|n\rangle + \frac{\omega_1}{2} e^{i\omega t}\langle i|J_-|n\rangle$$

$$\begin{aligned}
\Rightarrow a_i^{(1)}(t) &= \frac{\omega_1}{2i\hbar} J_{in}^{(+)} \int_0^t dt' \, e^{i(\omega_{in} - \omega)t'} + \frac{\omega_1}{2i\hbar} J_{in}^{(-)} \int_0^t dt' \, e^{i(\omega_{in} + \omega)t'} \\
&= \frac{\omega_1 J_{in}^{(+)}}{2\hbar(\omega_{in} - \omega)}\left\{1 - e^{i(\omega_{in} - \omega)t}\right\} + \frac{\omega_1 J_{in}^{(-)}}{2\hbar(\omega_{in} + \omega)}\left\{1 - e^{i(\omega_{in} + \omega)t}\right\}
\end{aligned}$$

Now

$$
\begin{aligned}
i\hbar\frac{da_i^{(2)}}{dt} &= \sum_j V_{ij}(t)e^{i\omega_{ij}t}a_j^{(1)}(t) \\
&= \frac{\omega_1}{2}\sum_j \left\{ J_{ij}^{(+)}e^{i(\omega_{ij}-\omega)t}a_j^{(1)}(t) + J_{ij}^{(-)}e^{i(\omega_{ij}+\omega)t}a_j^{(1)}(t) \right\}
\end{aligned}
$$

$$
\begin{aligned}
\frac{da_i^{(2)}}{dt} = \frac{\omega_1^2}{4i\hbar^2}\sum_j \Bigg\{ & J_{ij}^{(+)}\frac{e^{i(\omega_{ij}-\omega)t}J_{jn}^{(+)}}{(\omega_{jn}-\omega)}\left\{1-e^{i(\omega_{jn}-\omega)t}\right\} + \frac{J_{ij}^{(+)}J_{jn}^{(-)}e^{i(\omega_{ij}-\omega)t}}{(\omega_{jn}+\omega)}\left\{1-e^{i(\omega_{in}+\omega)t}\right\} \\
& + \frac{J_{ij}^{(-)}J_{jn}^{(+)}e^{i(\omega_{ij}+\omega)t}}{(\omega_{jn}-\omega)}\left\{1-e^{i(\omega_{jn}-\omega)t}\right\} + \frac{J_{ij}^{(-)}J_{jn}^{(-)}e^{i(\omega_{ij}+\omega)t}}{(\omega_{jn}+\omega)}\left\{1-e^{i(\omega_{jn}+\omega)t}\right\}\Bigg\} \qquad (10)
\end{aligned}
$$

We note that our final state $i = 3$ and the initial state $n = 1$. Because $j \neq i$ and $j \neq n \Rightarrow j = 2$. Thus $J_{jn}^{(-)} = J_{ij}^{(-)} = 0$. So only the first term of Eq.(10) will be non vanishing leading to

$$
\frac{da_3^{(2)}}{dt} = \frac{\omega_1^2}{4i\hbar^2}\frac{J_{32}^{(+)}J_{21}^{(+)}e^{i(\omega_{32}-\omega)t}}{(\omega_{21}-\omega)}\left\{1-e^{i(\omega_{21}-\omega)t}\right\}
$$

Using

$$
\begin{aligned}
\omega_{32} &= \omega_0 \\
\omega_{32}+\omega_{21} = \omega_{31} &= \omega_0+\omega_0' \\
\omega_{21} &= \omega_0'
\end{aligned}
$$

we have $J_{32}^{(+)} = J_{21}^{(+)} = \hbar\sqrt{2}$

$$
\frac{da_3^{(2)}}{dt} = \frac{\omega_1^2}{2\hbar i(\omega_0'-\omega)}\left\{e^{i(\omega_0-\omega)t} - e^{i(\omega_0+\omega_0'-2\omega)t}\right\}
$$

$$
\begin{aligned}
a_3^{(2)}(t) &= \frac{\omega_1^2}{2\hbar i(\omega_0'-\omega)}\int_0^t dt'\left\{e^{i(\omega_0-\omega)t'} - e^{i(\omega_0+\omega_0'-2\omega)t'}\right\} \\
&= \frac{\omega_1^2}{2\hbar(\omega_0'-\omega)}\left\{\frac{1-e^{i(\omega_0-\omega)t}}{(\omega_0-\omega)}\right\} + \frac{\omega_1^2}{2\hbar(\omega_0'-\omega)}\left\{\frac{1-e^{i(\omega_0+\omega_0'-2\omega)t}}{(\omega_0+\omega_0'-2\omega)}\right\}
\end{aligned}
$$

Now

$$
P_{1\to 3}(t) = |a_3^{(2)}(t)|^2
$$

$$
\begin{aligned}
P_{1\to 3}(t) = \frac{\omega_1^4}{4\hbar^2(\omega_0'-\omega)^2}\Bigg\{ & \frac{4\sin^2\frac{(\omega_0-\omega)t}{2}}{(\omega_0-\omega)^2} + \frac{4\sin^2\frac{(\omega_0+\omega_0'-2\omega)t}{2}}{(\omega_0+\omega_0'-2\omega)^2} \\
& + \frac{\left(1-e^{i(\omega_0-\omega)t}\right)\times\left(1-e^{-i(\omega_0+\omega_0'-2\omega)t}\right)}{(\omega_0-\omega)(\omega_0+\omega_0'-2\omega)} + \frac{\left(1-e^{-i(\omega_0-\omega)t}\right)\times\left(1-e^{i(\omega_0+\omega_0'-2\omega)t}\right)}{(\omega_0-\omega)(\omega_0+\omega_0'-2\omega)}\Bigg\}
\end{aligned}
$$

Let us simplify the last two terms

$$
\begin{aligned}
&= \frac{\left(2-e^{i(\omega_0-\omega)t}-e^{-i(\omega_0-\omega)t}+e^{i(\omega_0+\omega_0'-2\omega)t}-e^{-i(\omega_0+\omega_0'-2\omega)t}+e^{i(\omega_0'-\omega)t}+e^{-i(\omega_0'-\omega)t}\right)}{(\omega_0-\omega)(\omega_0+\omega_0'-2\omega)} \\
&= \frac{2\left(1-\cos(\omega_0-\omega)t-\cos(\omega_0+\omega_0'-2\omega)t+\cos(\omega_0'-\omega)t\right)}{(\omega_0-\omega)(\omega_0+\omega_0'-2\omega)}
\end{aligned}
$$

So

$$P_{1\to3}(t) = \frac{\omega_1^4}{\hbar^2(\omega_0' - \omega)^2}\left\{\frac{\sin^2\frac{(\omega_0-\omega)t}{2}}{(\omega_0-\omega)^2} + \frac{\sin^2\frac{(\omega_0+\omega_0'-2\omega)t}{2}}{(\omega_0+\omega_0'-2\omega)^2}\right.$$
$$\left. + \frac{(1-\cos(\omega_0-\omega)t - \cos(\omega_0+\omega_0'-2\omega)t + \cos(\omega_0'-\omega)t)}{(\omega_0-\omega)(\omega_0+\omega_0'-2\omega)}\right\}$$

It is obvious that $P_{1\to3}(t)$ diverges at $\omega = \omega_0'$, $\omega = \omega_0$, and $\omega = \frac{\omega_0+\omega_0'}{2}$. Thus, these are the frequencies at which resonant response occurs.

6. Photoelectric effect is the ejection of an electron from a system, because of its interaction with an incident radiation field. Calculate the cross-section for photoelectric effect for a hydrogen atom in its ground state, by taking the initial electronic state to be the $1s$ wave function of the hydrogen atom, and the final state to be a box normalized plane wave $\frac{1}{L^{3/2}}e^{i\mathbf{k}\cdot\mathbf{r}}$. The radiation field is represented by a plane wave of frequency ω, wave vector $\frac{\omega}{c}\hat{\mathbf{n}}$, polarized in the direction $\hat{\mathbf{e}}$.
Soln: We showed in the lectures that the absorption cross-section for a beam of photons of energy $\hbar\omega$, interacting with an electronic system, leading to a transition from the initial state $|n\rangle$ to the final state $|i\rangle$ is given by

$$\sigma_{n\to i}(\omega) = \frac{4\pi^2\alpha}{m^2\omega}|\langle i|e^{i\mathbf{k}_{ph}\cdot\mathbf{r}}\hat{\mathbf{e}}\cdot\mathbf{p}|n\rangle|^2\delta(\omega-\omega_{in}),$$

where $\mathbf{k}_{ph} = \frac{\omega}{c}\hat{\mathbf{n}}$ is the photon wave vector, $\omega_{in} = \frac{E_i - E_n}{\hbar}$, $\hat{\mathbf{e}}$ is the polarization direction of the photons, and it is assumed that $|n\rangle$ and $|i\rangle$ are discrete levels of the system. In photoelectric effect for the ground state of hydrogen atom $|n\rangle = |1s\rangle$, while $|i\rangle$, the final state of the electron is in the continuum, for which rigorous solutions are available. However, we will perform an approximate calculation assuming that energy of the photon is much larger than the ionization potential of the 1s state, i.e., $\hbar\omega \gg E_{1s}^{IP}$, so that the ejected electron wave function can be assumed to be a free-particle wave function

$$\langle\mathbf{r}|i\rangle = \frac{1}{L^{3/2}}e^{i\mathbf{k}\cdot\mathbf{r}},$$

where the wave function is assumed to be normalized in a cubic box of edge length L, with energy $E_i = \hbar^2k^2/2m = \hbar\omega + E_{1s}$. But, it is possible to have several $\mathbf{k}$ values for electron, for the same value of E_i, and we need to perform summation over all those states. Therefore

$$d\sigma_n(\omega) = \int_{\Delta\omega}\sigma_{n\to i}(\omega)d\omega = \frac{4\pi^2\alpha}{m^2\omega}|\langle i|e^{i\mathbf{k}_{ph}\cdot\mathbf{r}}\hat{\mathbf{e}}\cdot\mathbf{p}|n\rangle|^2\rho(\omega=\omega_{k1s}),$$

where $d\sigma_n(\omega)$ is the differential cross-section for emission of an electron in a small solid angle between Ω and $\Omega + d\Omega$, measured with respect to the direction $\hat{\mathbf{n}}$ of the photon beam, and the integral is over a frequency region of width $\Delta\omega$, centered at $\hbar\omega = E_i - E_{1s}$. Above $\rho(E)$ denotes the density of states of the free electron in the final state. But, for a 3D free electron

$$\rho(E_k) = \frac{d\Omega}{4\pi}\frac{m^{3/2}\sqrt{E_k}L^3}{\sqrt{2}\pi^2\hbar^2},$$

where $E_k = \hbar^2k^2/2m$, and the $1s$ wave function for an electron moving in the field of a nucleus of charge Z is given by

$$\langle\mathbf{r}|1s\rangle = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}e^{-Zr/a},$$

where a is the Bohr radius. With this, the differential cross section will be given by

$$\frac{d\sigma_{1s}(\omega)}{d\Omega} = \frac{e^2kZ^3}{2mc\hbar^2\pi^2\omega a^3}|\int e^{-i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}_{ph}\cdot\mathbf{r}}\hat{\mathbf{e}}\cdot\frac{\hbar}{i}\nabla e^{-Zr/a}d^3\mathbf{r}|^2.$$

One can evaluate the required integral to be

$$\int e^{-i\mathbf{k}\cdot\mathbf{r}+i\mathbf{k}_{ph}\cdot\mathbf{r}}\hat{\mathbf{e}}\cdot\frac{\hbar}{i}\nabla e^{-Zr/a}d^3\mathbf{r} = \hat{\mathbf{e}}\cdot\mathbf{k}\frac{8\pi Z\hbar}{a}\left(\frac{Z^2}{a^2}+q^2\right)^{-2},$$

leading to the final result

$$\frac{d\sigma_{1s}(\omega)}{d\Omega} = \frac{32e^2k(\hat{\mathbf{e}}\cdot\mathbf{k})^2}{mc\omega}\frac{Z^5}{a^5}\left(\frac{Z^2}{a^2}+q^2\right)^{-4}$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}_{ph} = \mathbf{k} - \frac{\omega}{c}\hat{\mathbf{n}}$, is called the momentum transfer.

7. A hydrogen atom in its ground state is placed between the plates of a capacitor, which applies the following time-dependent electric field

$$\mathbf{E} = \begin{cases} 0 & \text{for } t < 0 \\ \mathcal{E}_0 e^{-t/\tau}\hat{k} & \text{for } t > 0 \end{cases}$$

Using first-order time-dependent perturbation theory, calculate the transition probability $P_{1s\to 2p_0}(t \gg \tau)$, where $2p_0$ state corresponds to the $2p$ state with $m = 0$.

Soln: It is given that the hydrogen atom initially ($t = 0$) is in the ground state $|1s\rangle$, and finally in the state $|2p_0\rangle$. So in the first order of perturbation theory

$$a^{(1)}_{2p_0}(t) = \frac{1}{i\hbar}\int_0^t dt' \, e^{i(E^0_{2p}-E^0_{1s})t'/\hbar} V_{2p_0,1s}(t'),$$

where $V(t) = e\mathbf{E}\cdot\mathbf{r} = e\mathcal{E}_0 e^{-t/\tau} z$. Thus

$$\begin{aligned} a^{(1)}_{2p_0}(t) &= \frac{e\mathcal{E}_0\langle 2p_0|z|1s\rangle}{i\hbar}\int_0^t dt' \, e^{i(E^0_{2p}-E^0_{1s})t'/\hbar - t'/\tau} \\ &= \frac{e\mathcal{E}_0\langle 2p_0|z|1s\rangle}{i\hbar}\left(\frac{e^{i(E^0_{2p}-E^0_{1s})t/\hbar - t/\tau}-1}{i(E^0_{2p}-E^0_{1s})/\hbar - 1/\tau}\right). \end{aligned}$$

Therefore, the required transition probability is

$$\begin{aligned} P_{1s\to 2p_0}(t) &= |a^{(1)}_{2p_0}(t)|^2 \\ &= \frac{e^2\mathcal{E}_0^2|\langle 2p_0|z|1s\rangle|^2}{\hbar^2}\left(\frac{e^{i(E^0_{2p}-E^0_{1s})t/\hbar - t/\tau}-1}{i(E^0_{2p}-E^0_{1s})/\hbar - 1/\tau}\right)\left(\frac{e^{-i(E^0_{2p}-E^0_{1s})t/\hbar - t/\tau}-1}{-i(E^0_{2p}-E^0_{1s})/\hbar - 1/\tau}\right) \\ &= \frac{e^2\mathcal{E}_0^2|\langle 2p_0|z|1s\rangle|^2}{\hbar^2}\left(\frac{e^{-2t/\tau} - e^{-t/\tau}(e^{-i(E^0_{2p}-E^0_{1s})t/\hbar} + e^{i(E^0_{2p}-E^0_{1s})t/\hbar}) + 1}{(E^0_{2p}-E^0_{1s})^2/\hbar^2 + \frac{1}{\tau^2}}\right) \\ &= \frac{e^2\mathcal{E}_0^2|\langle 2p_0|z|1s\rangle|^2}{\hbar^2}\left(\frac{1 + e^{-2t/\tau} - 2e^{-t/\tau}\cos\frac{(E^0_{2p}-E^0_{1s})t}{\hbar}}{(E^0_{2p}-E^0_{1s})^2/\hbar^2 + \frac{1}{\tau^2}}\right). \end{aligned}$$

The matrix element $\langle 2p_0|z|1s\rangle$, can be calculated using Wigner-Eckart theorem, by realizing $z = \sqrt{\frac{4\pi}{3}} r Y^0_1(\theta,\phi)$

$$\langle 2p_0|z|1s\rangle = \sqrt{\frac{4\pi}{3}}\langle 2p_0|rY^0_1(\theta,\phi)|1s\rangle = \sqrt{\frac{4\pi}{3}}\langle 0100|0110\rangle\langle 1s||r|2p\rangle$$

but $\langle 0100|0110\rangle = 1$, and radial wave functions for H atom

$$R_{1s} = \frac{1}{2a_0^{3/2}}e^{-r/a_{a0}}, \; R_{2p} = \frac{1}{(2a_0)^{3/2}\sqrt{3}}\frac{r}{a_0}e^{-r/a_{a0}}$$

$$\implies \langle 2p_0|z|1s\rangle = \sqrt{\frac{4\pi}{3}}\frac{1}{4a_0^4\sqrt{6}}\int_0^\infty r^4 e^{-2r/a_0}dr = \sqrt{\frac{4\pi}{3}}\frac{1}{4a_0^4\sqrt{6}} \times \frac{a_0^5 4!}{2^5}$$

$$\implies \langle 2p_0|z|1s\rangle = \frac{a_0}{16}\sqrt{2\pi}.$$

Using this, we obtain the required transition probability to be

$$P_{1s\to 2p_0}(t) = \frac{2\pi e^2\mathcal{E}_0^2 a_0^2}{256\hbar^2}\left(\frac{1 + e^{-2t/\tau} - 2e^{-t/\tau}\cos\frac{(E^0_{2p}-E^0_{1s})t}{\hbar}}{(E^0_{2p}-E^0_{1s})^2/\hbar^2 + \frac{1}{\tau^2}}\right)$$

For $t \gg \tau$, we can take $t \to \infty$, limit for which $e^{-t/\tau} \to 0$, leading to

$$P_{1s\to 2p_0}(t \gg \tau) \approx \frac{2\pi e^2\mathcal{E}_0^2 a_0^2}{256\hbar^2}\left(\frac{1}{(E^0_{2p}-E^0_{1s})^2/\hbar^2 + \frac{1}{\tau^2}}\right)$$